RAPID, PORTABLE VOLTAMMETRIC TECHNIQUES FOR PERFORMING ANTIOXIDANT, TOTAL ACID NUMBER (TAN) AND TOTAL BASE NUMBER (TBN) MEASUREMENTS

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Abstract: This paper describes rapid voltammetric techniques for determining the antioxidant, total acid number (TAN), and total base number (TBN) measurements of a wide variety of oils and fluids. The voltammetric techniques require less than 1 milliliter (mL) of oil, 5 mL of acetone or ethanol solution, and less than 2 minutes for each analysis and can are performed in vials using inexpensive, portable instruments. In contrast to currently used TAN (ASTM Method 664) and TBN (ASTM Method 2896 or 4739) techniques, the voltammetric techniques do not involve titrations, and consequently, do not rely on endpoints which are operator dependent. Once prepared, the oil/analysis solution mixture can be analyzed several times (20 seconds per repeat analysis) to ensure the accuracy of the voltammetric analyses. The current ASTM methods require resampling followed by a new titration (requiring several minutes per titration) for duplicate analyses.

This paper also presents results for the voltammetric and ASTM method (TAN and TBN) analyses of various new, laboratory stressed, and authentic used fluids obtained from different types of normally and abnormally operating equipment. The evaluated oils and fluids include diesel engine oils obtained from test stands, phosphate ester based hydraulic fluids obtained from commercial airliners, and ester based turbine engine lubricating oils obtained from military and commercial aircraft. The results presented herein demonstrate that combined knowledge of the antioxidant/TAN/TBN (if applicable) measurements improves the capability of the analyst or equipment operator to evaluate the remaining useful life of the tested fluid as well as the condition of the operating equipment. Interrelationships among the different voltammetric analyses and wear debris analyses of the used oils and fluids are demonstrated and discussed.

Key Words: Antioxidant, Oil Analysis, Condition Monitoring, Remaining Useful Life, Total Acid Number, Total Base Number, Voltammetric Analysis

INTRODUCTION: Organic fluids are used in a wide range of applications in which the fluid experiences thermal/oxidative stresses. Depending on the application, different types of compounds are added to the fluid to enhance its performance. One type of fluid uses esters of

carboxylic acids fortified by antioxidants (aromatic amines) and antiwear (tricresyl phosphate) additives to meet the lubrication requirements of aircraft gas turbine engines. Another type of fluid uses esters of phosphic acid fortified by corrosion inhibitors (amines) to meet the non-flammability, lubrication requirements of commercial aircraft and industrial hydraulic systems. However, the majority of fluids use long chain hydrocarbons (petroleum or synthetic) fortified by antioxidants (hindered phenols), multifunctional antiwear additives (metal and non-metal dithio-phosphates) and corrosion inhibitors (amines) to meet the lubrication requirements of a wide range of industrial machinery and hydraulic systems. Compounds (calcium carbonate as well as overbased detergents and antiwear additives) are added to oils used in diesel and gasoline combustion engines (to neutralize sulfur and nitrogen acids caused by combustion of fuel) in addition to the antioxidant/antiwear/anti-corrosion additives.

During use in the operating equipment, the additives deplete at a rate dependent upon the environment experienced by the fluid [1]. For instance, the R&O (rust and oxidation inhibited) oils used in industrial gas and steam turbine engines are typically formulated with hindered phenol antioxidants and amine corrosion inhibitors. The hindered phenol antioxidants deplete at a faster rate than the corrosion inhibitors in the gas turbine system (thermal-oxidative environment) but deplete at a slower rate than the corrosion inhibitors in the steam turbine system (lower temperature, water present). Another example of competing depletion mechanisms occurs for the hindered phenol antioxidants and zinc dithiophosphate (ZDTP) antiwear additives used in hydrocarbon based hydraulic fluids. The phenol antioxidants deplete faster than the ZDTP antiwear additives in the thermal-oxidative environment of precision machining equipment (thermal-oxidative, low friction) but deplete slower than the ZDTP additive in high pressure pumps (thermal-oxidative, high friction).

Once the additive(s) decrease to a critical level, the lubricating/corrosion inhibiting/flowing capabilities of the fluid begin to decrease at an accelerated rate resulting in equipment damage, and possibly, equipment failure. To avoid equipment damage caused by fluid overusage, most condition monitoring programs detect fluid degradation using the total acid number (TAN) measurement technique (ASTM Method 664) which measures the accumulation of acids from fluid oxidation (fuel combustion) and hydrolysis. In the case of combustion engine oils, condition monitoring programs also employ total base number (TBN) measurements (ASTM Methods 664, 2896 or 4739) to determine the fluid's ability to neutralize corrosive combustion acids. In addition to fluid degradation, programs use analytical techniques to measure trace metal contents (additives, wear metal debris, dissolved metal from corrosion, etc.) of oil samples using atomic absorption (AA) or atomic emission (DCP or ICP) spectrometric techniques. [The discussion of metal analyses of fluids will be minimal in this paper except for wear metal debris increases caused by additive depletions.]

The main drawback of the TAN technique is its inability to predict the operating time from when the analyzed fluid was sampled until a fluid change will become necessary due to additive depletion, i.e., TAN techniques cannot predict the remaining useful life of a fluid. In addition to being non-predictive, the TAN analyses are affected by the operating conditions of the equipment (carboxylic acids from accelerated fluid oxidation volatilize) or by the additives. For instance, new fluids containing ZDTP antiwear additive have TAN values of 1-2 mg KOH/g of oil which

decrease (additive depletion) upon initial use, level off during further use (additive depletion compensated by oxidation acid increase), and then increase rapidly (oxidation acids accumulating). Consequently, measured increases in the TAN of a sampled oil may be due to fluid degradation (fluid being overused) or fluid replenishment (fluid being underused).

In contrast to fluid degradation techniques, analytical techniques which determine the additive (antioxidant, antiwear, anticorrosion) concentration of used oil samples are able to predict the operating time (assuming minimal fluid make-up) at which the additive will be totally depleted. However, the concentration at which the additive becomes ineffective (acid accumulation, wear debris or trace metal increase, etc.) will depend on the operating conditions of the fluid application. Historical relationships between additive concentration and fluid degradation need to be established so that percent remaining useful life (% RUL) plots can be established for each fluid application.

If fluid degradation does not occur until the additive is totally depleted, then the % RUL will be equal to the percent remaining antioxidant level. However, the 0% RUL (rapid degradation occurs) usually corresponds to 20-40% remaining antioxidant. In most cases the higher the temperature application, the larger the difference between 0% RUL and total antioxidant depletion. Also, other mechanisms such as hydrolysis, depletion of overbased additive, overheating (thermal) and so on may cause fluid degradation without affecting the antioxidant concentration.

Therefore, an oil analysis procedure which measures additive levels (% RUL) as well as fluid degradation [TAN and TBN (if applicable)] will afford the most accurate assessment of new and used fluids (and in numerous cases provide information on equipment health) regardless of the application. The combined additive/degradation measurement has the following capabilities:

(1) Quality assurance of incoming batches of lubricants - check type and concentration of additives, compare antioxidant packages of different manufacturers, etc.

(2) Determine correct oil change intervals - determine the depletion rate of the antioxidants and the antioxidant concentration at which the fluid degradation rate dramatically increases to predict correct oil change intervals for each piece of operating equipment.

(3) Extend oil change intervals - determine the depletion rate of individual antioxidants so that the selected antioxidants can be replenished to extend the useful life of the monitored lubricant.

(4) Detect abnormally operating equipment - once the normal depletion rates of the antioxidants have been established, accelerated antioxidant depletion rates can be used to detect abnormally operating equipment.

(5) Monitor non-oxidative degradation mechanisms such as hydrolysis, overheating, and acid accumulation from combustion gases.

TECHNOLOGY DESCRIPTION: Although, numerous long-term oxidation tests are available to perform antioxidant depletion (% RUL) measurements of different type fluids, they are unsuitable for routine use. Voltammetric techniques [1-4] are capable of performing rapid (less than 1 minute) antioxidant analyses but are unable to perform TAN or TBN measurements. Therefore, research was performed to develop TAN and TBN methods that could be performed on small, portable voltammetric instruments designed to perform antioxidant analyses.

The main objections to performing TAN (ASTM 664) and TBN (ASTM 2896 and 4739) methods are the methods require time consuming titrations with hazardous solvents (toluene, chlorobenzene, acetic acid, etc.). The TAN and TBN titrations are performed until an endpoint (rapid change in pH or color change with single drop of titrant) or predetermined pH value (established with buffers) is reached. Since the endpoint or predetermined pH value is not always distinct or stable, the TAN and TBN values tend to be highly operator dependent, especially TBN measurements of used oils. Also, in the case of ester based fluids, chemical reactions may occur between the basestock and titrant leading to superficially high TAN and TBN numbers.

The main basis for the voltammetric TAN technique is the use of electroactive (detected by voltammetry) compounds that become non-electroactive (not detected by voltammetry) in the presence of accumulated acids (TAN method). For the TBN technique, insoluble compounds which become soluble and electroactive in the presence of hydrochloric acid (TBN titrant) were used. In the voltammetric TAN and TBN techniques, the concentration of the electroactive species is determined before and after adding, then shaking the oil sample with the voltammetric solution. The difference in electroactive species concentration and the amount of oil added is then used to calculate the TAN or TBN of the oil sample. Since the voltammetric analysis detects (does not titrate) the concentration of the electroactive species, multiple analyses can be made on the same prepared solution to increase the accuracy of the voltammetric TAN and TBN results. The ASTM methods require resampling of the oil to perform duplicate analyses increasing the time requirements and waste of the TAN and TBN methods. In addition to other advantages, the voltammetric TAN and TBN techniques use smaller quantities (5 mL vs up to 100 mL) of less toxic solvents (ethanol or acetone vs toluene, chlorobenzene, acetic acid) compared to the ASTM methods.

This paper also presents results for the voltammetric and ASTM method (TAN and TBN) analyses of various new, laboratory stressed, and authentic used fluids obtained from different types of normally and abnormally operating equipment. The evaluated oils and fluids include diesel engine oils obtained from test stands, phosphate ester based hydraulic fluids obtained from commercial airliners, and ester based turbine engine lubricating oils obtained from military and commercial aircraft. The results presented herein demonstrate that combined knowledge of the antioxidant/TAN/TBN (if applicable) measurements improves the capability of the analyst or equipment operator to evaluate the remaining useful life of the tested fluid as well as the condition of the operating equipment. Interrelationships among the different voltammetric analyses and wear debris analyses of the used oils and fluids are demonstrated and discussed.

EXPERIMENTAL: Lubricating Oils. The used lubricating oils and fluids analyzed in this paper were obtained from normally and abnormally operating equipment as well as laboratory stressing tests and diesel engine test stands. Several new oils and fluids were also analyzed. The types of oils and fluids analyzed included: aircraft gas turbine engine oils (carboxylate ester based), aircraft hydraulic fluids (phosphate ester based) and diesel engine oil (hydrocarbon based).

ASTM TAN and TBN Methods. The ASTM TAN and TBN results reported here in were performed by industrial oil analysis laboratories from which the used lubricants and fluids were obtained.

Voltammetric Additive Analyses. The voltammetric method was performed with a commercially available voltammograph equipped with a digital readout, stripchart output and electrode system (glassy carbon working electrode, a platinum wire reference electrode, and a platinum wire auxiliary electrode). A fresh oil typical of the application (100% standard) and the solvent system (0% standard) were used to calibrate the voltammetric instrument for % remaining a. :oxidant determinations.

The oil samples (100 - 500 μL) were diluted with acetone or ethanol containing a dissolved electrolyte and a suspended solid substrate. For aromatic amine type antioxidants the solvent system was acetone and the electrolyte was a neutral salt. For hindered phenol-type antioxidants and phenol degradation products the solvent system was water/ethanol and the electrolyte was an inorganic base. For zinc dialkyldithiophosphate type additives the solvent system was a water/acetone solution and the electrolyte was a neutral salt. When the oil/solvent/solid substrate mixture was shaken, the insoluble oil coated the solid substrate and upon standing the agglomerated particulates quickly settled out to produce a clear solution for analysis. The voltage of the auxiliary electrode was scanned from 0.0 to 1.0 V at a rate of 0.5 V/second. The height of the peaks produced by the voltammetric method were then used to evaluate the remaining additives of the used oil samples.

Voltammetric TAN Analysis. The voltammetric method was performed with the same voltammetric analyzer described for voltammetric additive analysis. The system was calibrated for TAN measurements as shown in Figure 1. The blank water/ethanol solution containing overbased phenol or phenyl phenol) was analyzed with the described voltammetric analyzer to produce the first peak (due to overbased phenol) in Figure 1. This peak height (analyzer reading = 520) represents a TAN value of 0.0 mg KOH/g of oil. To show the repeatability of the test, the same blank was reanalyzed to produce the second peak in Figure 1 (analyzer reading = 515). To the same blank solution, 50 μL of a 0.1N HCl in water solution was added and shaken for 3 seconds. The third peak in Figure 1 (analyzer reading = 140) represents the overbased phenol unreacted by the added acid and corresponds to a value of 0.28 mg of KOH. When the same experiment was repeated with a second blank and 50 μL of a 0.1N octanoic acid in water solution, the vial had to be shaken for 10 seconds to get complete reaction (peak decreased on second analysis after additional shaking). The peak produced by the octanoic acid was similar to the third peak in Figure 1 and had an analyzer reading of 130.

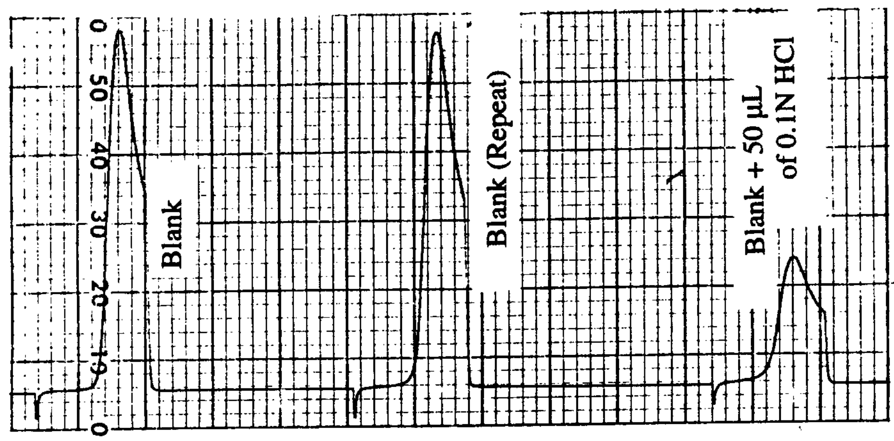

Figure 1. Voltammograms produced by analysis of the blank, repeat analysis of the blank, and analysis of the blank after addition of 50 µL of 0.1N HCl in water solution.

Therefore, the voltammetric TAN detects strong and weak acids equally well and can be used for qualitative comparisons of acid strength, i.e., if peak height obtained after 3 seconds of shaking does not change with additional shaking all of the detected acid is strong (mineral acid), if the peak height decreases substantially upon additional shaking a weak acid (carboxylic acid) is present. To calculate the TAN of a fluid sample using the data from Figure 1 the following equations are used:

$$\text{Calibration} = \frac{50\mu\text{L of } 0.1\text{ N acid}}{\text{Blank Reading - Acid Reading}} = \frac{0.28\text{ mg of KOH}}{520 - 140} = 7.4 \times 10^{-4}\ \frac{\text{mg of KOH}}{\text{readout unit}}$$

$$\text{TAN (mg of KOH / g of oil)} = \frac{\text{Blank Reading - Sample Reading}}{\text{Weight of Sample}} \times 7.4 \times 10^{-4}\ \frac{\text{mg of KOH}}{\text{reading unit}}$$

Voltammetric TBN Analysis. The voltammetric method was performed with the same voltammetric analyzer described for voltammetric additive analysis. The system was calibrated for TBN measurements in a similar manner to the TAN method. The blank was prepared by dispensing the reaction solution (water/ethanol solution containing HCl acid) into a vial containing copper powder. The solution/powder mixture was shaken for 10 seconds and allowed to sit undisturbed for 5 seconds to allow the powder to settle. The solution was then analyzed with the described voltammetric analyzer. The produced peak(analyzer reading = 1550) represents a TBN value = 0 mg of KOH/g of oil. The TBN standard was then prepared by dispensing the reaction solution and an oil (200 µL) of known TBN (usually TBN = 13) into a vial. The reaction solution/oil mixture was then shaken for 20 - 30 seconds and allowed to sit undisturbed for 5 seconds. Since ZDTP species produce peaks in the same area of the TBN method, the solution is analyzed for additive content and to establish the baseline for the TBN calculations. The reaction solution is then poured into a vial containing copper powder and

shaken for an additional 10 seconds to react any remaining HCl. The vial is allowed to sit undisturbed for 5 seconds then analyzed to produce the peak representative of a TBN value = 13 mg of KOH/g of oil (standard).

The oil samples to be analyzed for TBN are then analyzed in a manner similar to the calibration standard provided the samples' TBN values are below 13. For samples with TBN values between 13 and 52 mg of KOH/g, 50 μL samples are used. The TBN value of the oil sample is then calculated in the following manner:

$$\frac{\text{TBN of Standard}}{\text{Blank reading - Standard reading}} \times \frac{200\ \mu\text{L}}{\text{Oil sample size}(\mu\text{L})} = \frac{\text{TBN Value}}{\text{Unit Reading}}$$

$$\underset{\text{(mg KOH/g of oil)}}{\text{TBN value of oil sample}} = \text{(Sample reading - Baseline reading)} \times \frac{\text{TBN Value}}{\text{Reading Unit}}$$

RESULTS AND DISCUSSION: To initially evaluate the capabilities of the combined voltammetric additive/TAN/TBN measurements a wide range of new and used oils and fluids were analyzed. The used analyzed oils and fluids were obtained from laboratory engine test stands and stressing tests as well as normally and abnormally operating equipment.

Diesel Engine Oils. Of the numerous applications evaluated for this paper, the combined voltammetric analyses have the greatest potential benefit for diesel engine oils. As opposed to other analytical techniques, voltammetric analyses are not limited by the soot levels found in most used diesel engine oils. To evaluate the voltammetric additive/TAN/TBN potential for analyzing diesel engine oils, used engine oils were obtained from an extended IIIe engine test (test usually terminated at 48 hours). The voltammetric additive analyses and the ASTM TAN/TBN measurements were made by the laboratory personnel performing the engine test. The voltammetric TAN/TBN measurements were performed by the author. The resulting voltammetric and ASTM measurements of the new and used diesel engine oils were plotted versus engine operating time as shown in Figure 2. The results in Figure 2 show that the voltammetric and ASTM TAN measurements are in good agreement with the voltammetric values being slightly lower during the useful life of the oil (TAN values stable). The lower voltammetric TAN values are attributed to the fact that the voltammetric test detects the overbased additives (ZDTP,detergents,etc) to a lesser extent than the ASTM method. The results in Figure 2 also show that the voltammetric and ASTM TBN measurements are also in good agreement. The difference between the TBN tests after 48 hours is attributed to the fact that the voltammetric test is unaffected by the organic acids produced by oxidation but the ASTM method is buffered by the produced organic acids resulting in superficially high values.

In addition to the TAN/TBN measurements, the results in Figure 2 show that the voltammetric ZDTP analyses are the only analyses capable of determining the remaining useful life (RUL) of the oil being tested in the engine test. The oxidative RUL of the oil ends (TAN increases) when the ZDTP depletes to approximately 15% of its original concentration. A dramatic increase in the Fe concentration occurred (not plotted) at a ZDTP level of 10%, indicating the initiation of accelerated wear in a diesel engine can be predicted by the voltammetric ZDTP analyses.

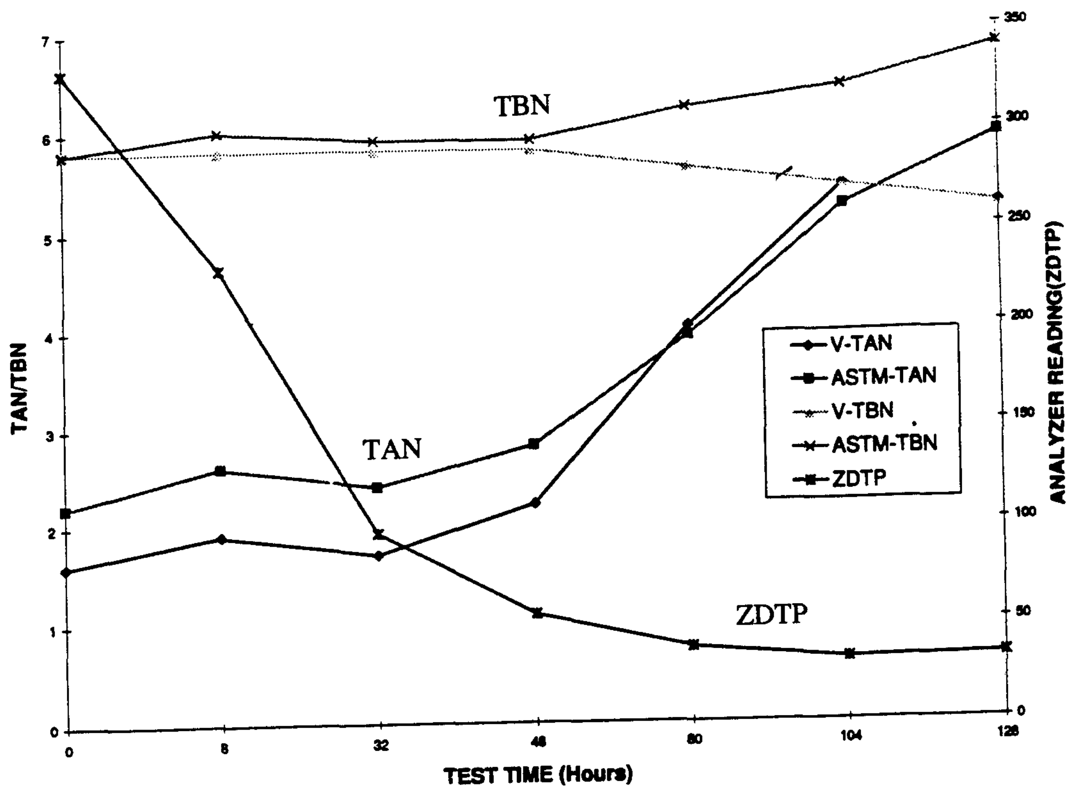

Figure 2. Plots of voltammetric and ASTM analyses versus engine test time for used diesel engine oils obtained from an extended IIIe engine test.

Therefore, the results in Figure 2 as well as additional evaluations [5] of used oils obtained from normally operating diesel and gasoline engines demonstrate that the combined voltammetric additive/TAN/TBN measurements provide the user with on-site capabilities to monitor both the RUL and condition of used diesel engine oils with minimal time and cost requirements. The results in Figure 2 also indicate that the voltammetric TBN values are more accurate than the ASTM TBN values for used diesel engine oils. The accuracy of voltammetric TAN results can be improved by subtracting out the additive concentrations detected by the voltammetric additive analyses.

Aircraft Turbine Engine Oils. As opposed to the diesel engine oils, aircraft turbine engine oils operate in a clean environment and are not subject to combustion acids, coolant leaks, soot, and so on. Therefore, the aircraft oils are not formulated with overbased detergents and calcium carbonates, and consequently, do not have a meaningful TBN value.

Previous research [2-4] has shown that voltammetric additive (aromatic amine antioxidants) analyses are able to detect abnormally operating aircraft engines. In particular, C-130 transport and commercial airliner engines experiencing severe oxidation due to cracked seals were detected by voltammetric additive analysis prior to accelerated wear and component failure. In

fact, the results from the prevoius studies indicated that oil degradation was the main failure mechanism for C-130 engines explaining the inability of spectrometric oil analysis to detect wear prior to engine failure [6].

In contrast to C-130 transport oil degradation mechanisms, oil samples from military fighters and commercial airliners have shown indications of overheating (e.g., F-16 black oil samples). The overheating at a hot spot causes coke formation with only minor decreases in the antioxidant level of the bulk oil. Consequently, additive analysis is ineffective in detecting the coking process. If allowed to continue without detection, the coke buildup will eventually break lose clogging oil jets and other small orifices resulting in decreased oil flow and lubricant starvation of the bearings. Previous studies [2] have shown that the conductivity of the oil increases dramatically during the coking process indicating polar species, possibly acidic species, are produced by the coking process.

Therefore, twenty oil samples obtained from normally and abnormally operating commercial airliner engines were analyzed for additive and TAN using the voltammetric analyzer. The results in the table below indicate that the majority (15 samples) of the oil samples have antioxidant levels greater than 90% and TAN values below 0.3 mg of KOH/g. The high oil makeup rates of the aircraft engines account for the high additive, low TAN measurements. Of the other 5 samples, two oils show significant additive depletion with minimal TAN values; these samples are in the early stages of accelerated oxidation (cracked seal) but have not reached rapid acid accumulation, i.e., % RUL > 0 (Figure 2) [records were not available for confirmation]. The other three oils show significant TAN value increases without significant antioxidant depletion; these samples are experiencing varying degrees of overheating. Conductivity [2] measurements detected overheating in samples 18-20 and airline maintenance personnel confirmed maintenance action had been required.

COMPARISON OF VOLTAMMETRIC ADDITIVE
AND TAN MEASUREMENTS FOR USED COMMERCIAL AIRLINE ENGINE OILS

Sample No.	% Antioxidant Remaining	TAN Value (mg KOH/g oil)
1-15	92-98	0.13 - 0.28
16-17	56-70	0.38, 0.31
18-20	81-85	1.1 - 2.8

Therefore, the results in the above discussion indicate that combined voltammetric additive/TAN measurements enables the user to better evaluate the RUL and condition of used aircraft oils by detecting two kinds of oil degradation mechanisms; accelerated oxidation (additive depletion) and coking (TAN increase). Long-term storage of aircraft oils can cause hydrolysis of the ester basestock which produces organic acids, and consequently, can also be detected by voltammetric TAN measurements.

Phosphate Ester Based Hydraulic Fluids: In contrast to hydrocarbon based hydraulic fluids, the fluids used in commercial aircraft hydraulic systems have phosphate ester basestocks. The

phosphate esters are used in aircraft hydraulic systems because they are fire resistant in comparison to hydrocarbon oils. Also, the phosphate esters don't require antiwear additives (e.g., ZDTP) due to their inherent lubricity. However, the phosphate esters undergo hydrolysis, oxidation, and thermal degradation to produce corrosive acids and phenolic compounds. Contamination of the hydraulic fluids with turbine engine oils is also a concern for operators of aircraft.

To evaluate the capabilities of the voltammetric analyses for phosphate ester hydraulic fluids, fresh fluids and authentic used fluids obtained from commercial aircraft hydraulic systems were analyzed. The voltammograms produced by two widely used phosphate ester hydraulic fluids and a suspect used hydraulic fluid are shown in Figure 3. The results in Figure 3 show that the two fresh fluids produce distinctly different spectra and that one of the used hydraulic fluids appears to be aircraft oil. The voltammetric analyses of the used phosphate esters showed that the amines decreased, and the phenolic degradation compounds increased dramatically, with use. The voltammetric analyses were in good agreement with the total acid number (ASTM Method D-664) and trace metal (e.g., Fe, Cu, etc.) measurements of the used fluids.

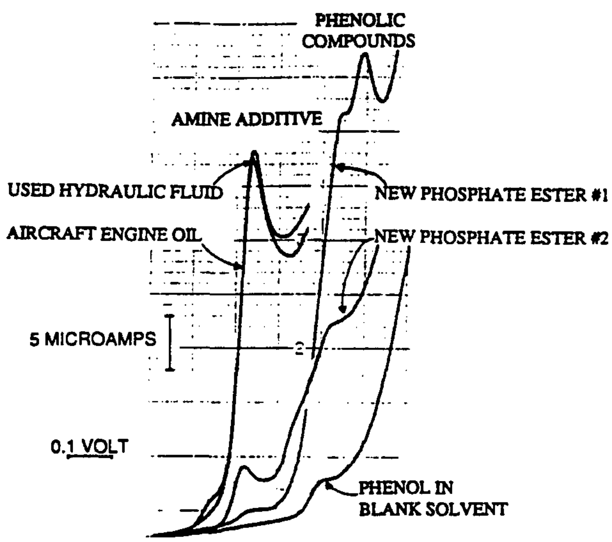

Figure 3. Voltammograms of two fresh and one suspect used phosphate ester hydraulic fluid in comparison to fresh aircraft engine oil.

To evaluate the voltammetric TAN method, the used fluids were analyzed and the results are plotted in Figure 4 versus the ASTM TAN values. The results in Figure 4 show that the voltammetric TAN values are in good agreement with the ASTM TAN values once an offset of 0.6 mg KOH is employed. The higher voltammetric TAN values for the phosphate ester fluids are caused by the phenolic species (initially present and produced during use) detected in the fluids (Figure 3) and can be compensated using the voltammetric additive analyses.

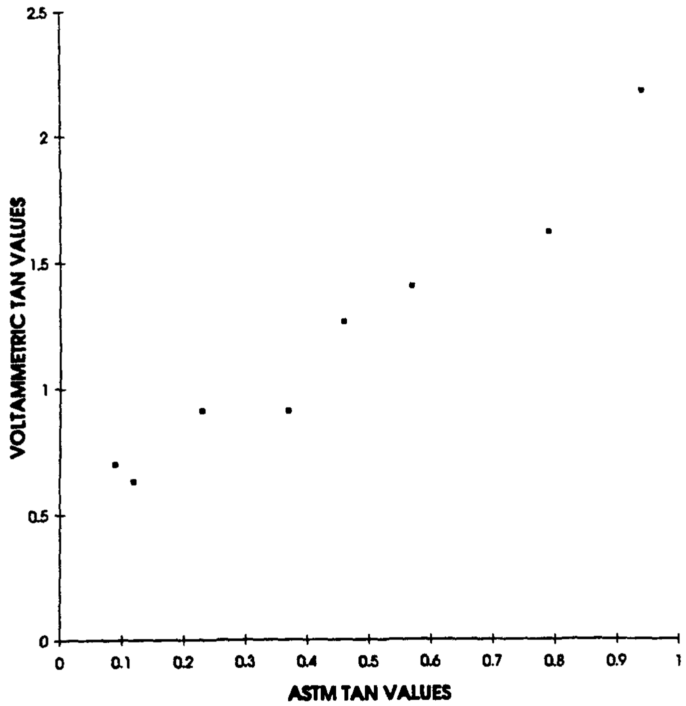

Figure 4. Plots of voltammetric TAN value versus ASTM TAN value for fresh and used phosphate ester hydraulic fluids obtained from a normally operating aircraft hydraulic system.

Therefore, these results indicate voltammetric additive/TAN measurements have great potential for monitoring the RUL and condition of phosphate ester hydraulic fluids. Whether monitoring phenol degradation products detected by voltammetry are of importance to operating efficiency (responsible for deposits on servo values) or for adjusting the voltammetric TAN values has yet to be determined.

SUMMARY: The initial results presented in this paper demonstrate that combined knowledge of the additive/TAN/TBN (if applicable) measurements improves the capability of the analyst or equipment operator to evaluate the RUL and condition of the tested fluid as well as the condition of the operating equipment. The results indicate that for diesel engine oils depletion of the ZDTP additive and for aircraft engine oils (e.g., C-130 aircraft oils) depletion of the antioxidant (and resulting basestock degradation) allow accelerated wear to occur. Consequently, voltammetric analyses can be used to aid in the determination of the wear mechanisms detected by spectrometric oil analysis programs. Present work with the combined additive/TAN/TBN analysis procedure includes industrial steam and gas turbine oils, mineral oil based hydraulic fluids, automotive engine oils and transmission fluids, water based metal working fluids and fuels (jet, diesel engine, and gasoline).

References

1. Kauffman, R. E., "Remaining Useful Life Measurements of Diesel Engine Oils, Automotive Engine Oils, Hydraulic Fluids, and Greases Using Cyclic Voltammetric Methods," Lub. Eng. 51(3), pp 223-229 (1995).

2. Kauffman, R. E., "On-Line and Off-Line Techniques for Monitoring the Thermal and Oxidative Degradation of Aircraft Turbine Engine Oils - Part 1: Laboratory Evaluations," Lub. Eng., 51(11), pp 914-920 (1995).

3. CRC Handbook of Lubrication and Tribology, Volume III Monitoring, Materials, Synthetic Lubricants, and Applications," Rapid Determination of Remaining Useful Lubricant Life, pp 89-100, Editor E. Booser, CRC Press, Ann Arbor MI (1994).

4. Kauffman, R. E. and Rhine, W. E., "Assessment of Remaining Lubricant Life," Report No. AFWAL-TR-86-2024, November 1986.

5. Kirkpatrick, J. F., "Diagnostic Tools for Reciprocating Engine Cogeneration Systems, Phase I," Gas Research Institute Report No. GRI-90/0022, January 1990.

6. Hancock, D. O. and Synovec, R. E., "Early Detection of C-130 Aircraft Engine Malfunction by Principal Component Analysis of the Wear Metals in C-130 Engine Oil," Appl. Spect. 43(2), pp 202-208 (1989).